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Mechanism of Reinforcement of Rubber with Hard Clay

Infrared Studies of Rubber-Fillers Systems*

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The mechanism of reinforcement of rubber with hard clay was studied by the infrared absorption spectra. The heat treatment of clay at the temperature up to 400°C gave no effect on the mechanical strength of the rubber. Further increase in the heating temperature resulted in remarkable decrease in the reinforcing ability of the clay. The particle size, state of dispersion in rubber, specific surface area, crystallinity, and the thermal analysis of the heat-treated clay were studied. The shape, size, and dispersability of the particles were not changed by the heat-treatment. The crystal structure was destroyed by heating at the temperature higher than 400°C with escape of structural water. The measurements of infrared absorption spectra were carried out for the hard clay itself and the hard clay dispersed in the rubber. One of OH bands of 3700 cm^{-1} was changed when the clay was mixed in rubber. This absorption peak was assigned to OH vibration on the lateral surface of kaolinite crystal. The reinforcing effect of kaolinite is intimately related to the interaction between the OH on the lateral surface and the rubber molecules. The reinforcing ability of clay is, therefore, lost by heating owing to the destruction of crystal structure.

1. INTRODUCTION

The mechanism of reinforcement of rubber with fillers has not yet been clarified. It is highly probable that a network structure is formed by the adsorption or chemical bonding between the functional radicals on the surface of particles of filler and the rubber molecules. It has been suggested[1] that a chemical bonding is formed between quinone or hydroquinone radicals on the surface of carbon black particles and saturated or unsaturated side chains of rubber molecules. The hydrogen bonding may also be formed between the free OH radicals on the surface of colloidal silica particles and the end groups of polymer. A hypothesis that the colloidal silica is a free radical acceptor, having ability to combine with the polymer, has also been proposed[2].

The synthetic rubber is reinforced remarkably by hard clay, a kind of kaolinite. In the present paper, the changes of physical properties of the hard clay by heat treatment are studied in relation to the reinforcing effect on the synthetic rubber. The mechanism of the reinforcement is discussed in detail.

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2. SAMPLES

The hard clay used was a product of South Eastern Co., Ltd, produced in Aiken, Carolina, U.S.A. The electronmicrographs of the sample are shown in Fig. 2(a). As is seen in the figure, the sample was composed of hexagonal plane crystals of kaolinite of $0.1-2\mu$ in size. The synthetic rubber, SBR 1502, was used, the composition of which is shown in Table 1.

3. EXPERIMENTAL RESULTS

3.1 Heat Treatment of Clay and the Changes of Physical Properties of Rubber reinforced with it

The hard clay was heat-treated at 200, 400, 600, and 800°C, and the tensile

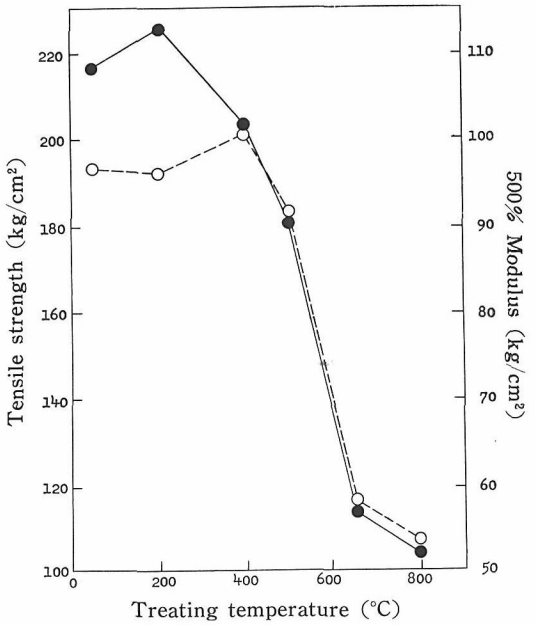


Fig. 1. Relation between treating temperature of hard clay and mechanical strength of reinforced rubber.

(a) (b) (c)

Fig. 2. Electronmicrographs of heat-treated clay.
(a) Untreated. (b) Heated at 400°C. (c) Heated at 800°C. (×18,000)

Table 1.

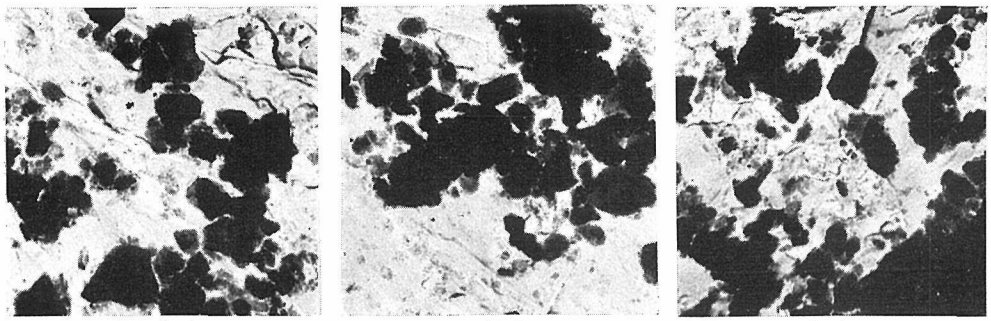
SBR 1502	100.0
Zinc Oxide	5.0
Stearic Acid	1.0
Sulfur	2.0
Promoter DM	1.5
Promoter M	0.5
Diethyleneglycol	3.0
Hard Clay	100.0

40 lb/in^2, press-vulcanized for 20 min.

strength and 500% modulus of SBR reinforced with the heat-treated clay were measured. The results are shown in Fig. 1. As is seen in the figure, both the tensile strength and the modulus were slightly increased by the heating at 200~400°C. When the heating temperature was raised to higher than 400°C, they decreased remarkably, and reached a stationary value at the temperature higher than 600°C. The physical properties of heat-treated clay and its state mixed in rubber were examined by various methods.

3.2 Electronmicrographic Observation of Shape, Size, and State of Dispersion of Heat-Treated Clay in Rubber

The electronmicrographs of the heat-treated clay are shown in Fig. 2 together with those of untreated sample. As is clearly seen in the figure, the sintering and aggregation of particles not observed. Even by the heating at 600°C, the shape of hexagonal plate was preserved. No crystal pattern was, however, observed by the selected-area electron diffraction method when the heating temperature was higher than 600°C. The particle size distribution was not determinable from these photographs since the grain size was not uniform and a number of aggregated were present. The electronmicrographs of clay particles dispersed in the rubber were obtained by the replica method, and the size distribution of aggregates was measured by using 400 aggregates. The photographs of replica are shown in Fig. 3, and the size



(a) (b) (c)

Fig. 3. Dispersion state of heat-treated clay in rubber, electronmicrographs of replica. (a) *Untreated clay.* (b) *Clay heated at 400°C.* (c) *Clay heated at 800°C.* (×18,000)

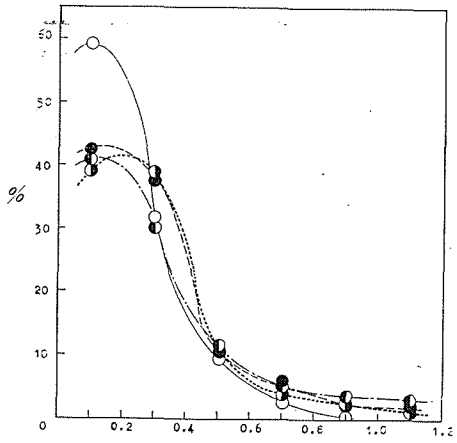


Fig. 4. Particle size distribution of heat-treated clay in rubber.
Untreated {clay itself ——○—— in rubber - - -●- - - Heat-treated {400°C ·····◑····· 800°C -·-·◐-·-·-

distribution of aggregates of heat-treated clay dispersed in the rubber are plotted in Fig. 4. As is seen in the figures, the size distribution was not uniform, and the grains had not the definite shape. The heat treatment gave no perceptible effect on the dispersion state.

3.3 Change of Specific Surface Area of Clay by Heat Treatment

The specific surface area of heat-treated clay was measured by the soap titration method using sodium stearate[4]. For the study of interaction between the surface of particles of filler and molecules of polymer such as rubber, the use of soap for the determination of surface area is more profitable than that of N_2 gas in the BET method. The specific surface area

Table 2.

Treating temperature	Specific surface area (m^2/g)
Untreated Sample	2.05
400°C	2.47
800°C	3.56

obtained is shown in Table 2. The specific surface area increased with the heating temperature.

3.4 Change of Crystal Structure by Heat Treatment

The X-ray diffraction of heat-treated clay is shown in Fig. 5. The untreated clay showed the diffraction pattern of kaolinite of low crystallinity. The heating at 400°C almost no change. At 600°C, the crystallinity was lowered, and the crystal structure was completely destroyed by the heating

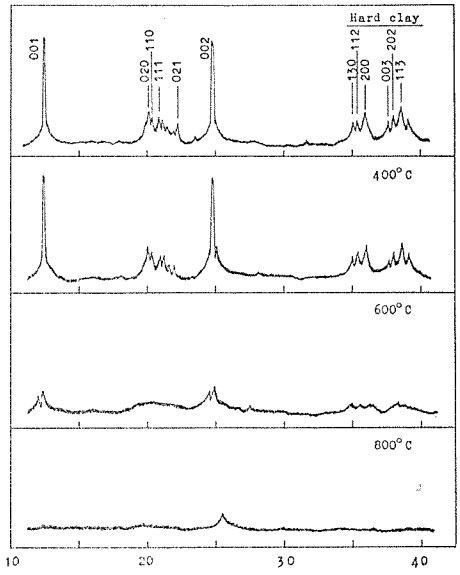


Fig. 5. X-ray diffraction of heat-treated clay

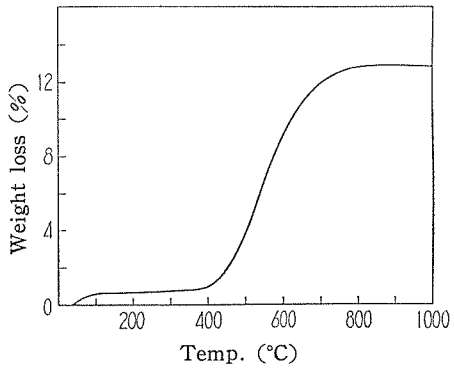


Fig. 6. Thermal analysis of hard clay.

at 800°C.

3.5 Thermal Analysis

The thermal analysis of clay was made with an autorecording thermobalance. The results are shown in Fig. 6. The weight loss of 1% up to 100°C was due to the escape of occluded and absorbed water. The loss increased rapidly at 450°C, and the weight reached a constant value at 700°C. The loss in the higher temperature amounted to 12% of the total weight of sample.

3.6 Heat Treatment and Infrared Absorption Spectra

The infrared absorption spectra were obtained by the nujol method using NaCl prism. The changes of spectra by the heat-treatment are shown in Fig. 7. The assignments of the absorption band are given in Table 3. Up to

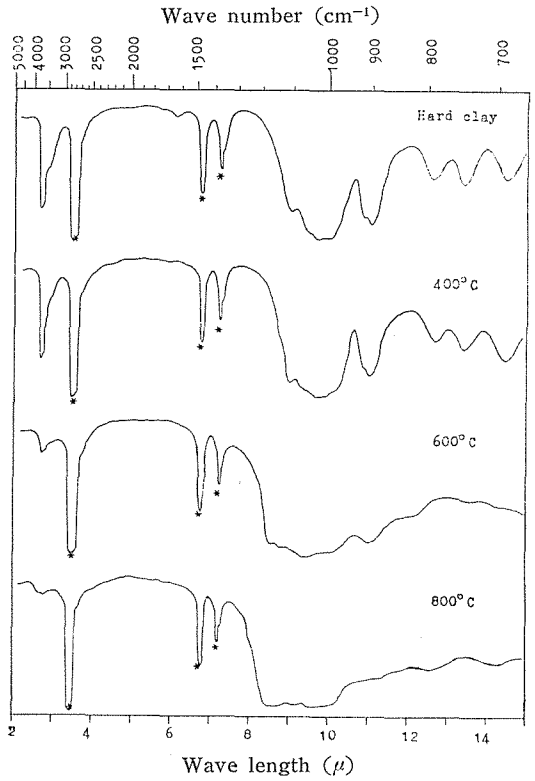


Fig. 7. Infrared absorption spectra of heat-treated clay.

Table 3.

Wave number (cm^{-1})	
3600～3700	O-H
3430	O-H (Interplanar water)
1120～1000	Si-O
935, 920	O-Al-OH
790	——
750	Si-O-Al
690	Si-O

400°C, the spectra were those of kaolonite. When the heating temperature was raised to 600°C, the intensity of OH band at 3650 cm^{-1} decreased, Si-O absorption peak appeared newly at 1200 cm^{-1}, and the absorption at 910 cm^{-1} disappeared. The kaolinite in layer structure was decomposed into silica and alumina at this temperature. The heating at 800°C enhanced this decomposition.

In general, the absorption band of Si-O at 1000～1100 cm^{-1} of clay does not appear as sharp peak. The characteristic absorption of clay mineral is that of OH band appearing in OH vibration region at 3500～3700 cm^{-1}. The

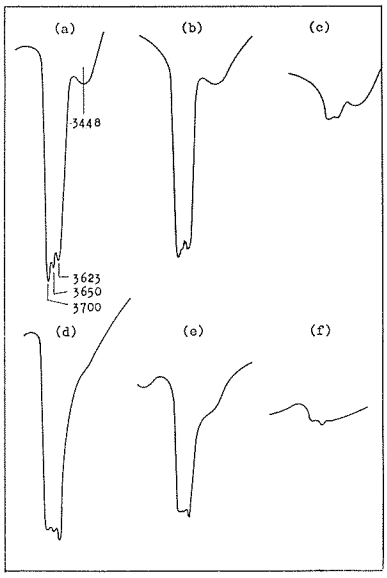


Fig. 8. Changes of OH absorption bands by heat-treatment and on mixing in rubber.
(a) Untreated clay. (d) Untreated clay in rubber.
(b) Clay heated at 400°C. (e) Clay herated at 400°C, in rubber.
(c) Clay heated at 600°C. (f) Clay heated at 600°C, in rubber.

change of OH band was measured with LiF prism. The result is shown in Fig. 8. The absorption band of OH was divided into four peaks, which became faint by the heating at 600°C, and disappeared at 800°C. The assignments of these absorptions will be given below.

3.7 Infrared Absorption Spectra of Rubber Reinforced with Clay

In order to study the interaction between the filler and the rubber, the measurement of infrared absorption spectra of the reinforced rubber was made by using thin sections obtained by the freezing microtome[5]. The result is shown in Fig. 9. The infrared absorption of masticated rubber compounded with clay was the superposition of that of SBR and of the kaolinite. In the spectra of vulcanized rubber, on the contrary, the absorption peak of C=O at 1710 cm^{-1} disappeared and that of $C\begin{matrix}O\\O\end{matrix}$ at 1540 cm^{-1} appeared newly. The absorption of OH near 3500 cm^{-1} of the rubber mixed with clay obtained with LiF prism is shown in Fig. 8. The most intense absorption peak of clay at 3700 cm^{-1} became weak in the rubber, and instead the absorption at 3623 cm^{-1} became most intense. The clay after at 400°C gave similar spectra. These absorption peaks disappeared when the clay was heated at 800°C.

4. DISCUSSION

The perfect crystal of kaolinite has a composition of $Si_4\ Al_4\ O_{10}\ (OH)_8$

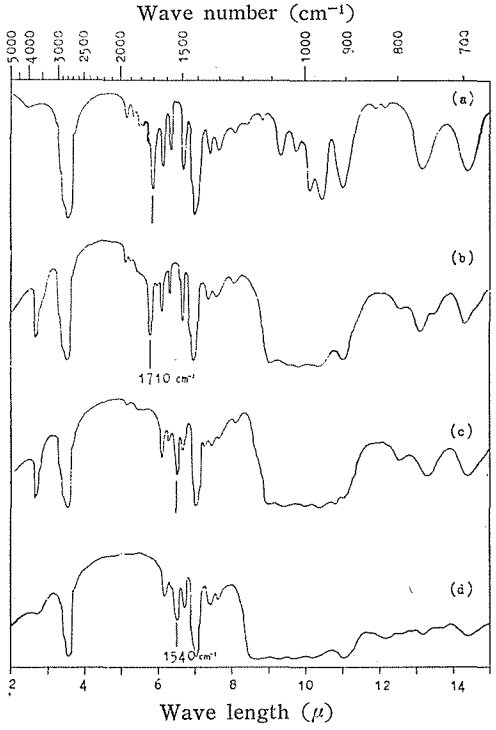


Fig. 9. Infrared absorption spectra of rubber mixed with heat-treated clay.
(a) SBR 1502.
(b) Untreated clay-unvulcanized rubber.
(c) Untreated clay-vulcanized rubber.
(d) Clay heated at 800°C–vulcanized rubber.

(SiO_2 46.54%, Al_2O_3 39.50%, H_2O 13.96% by weight). The ignition loss of 12% at 500°C is due to the escape of structural water. As is proved by X-ray diffraction and infrared absorption spectra, the kaolinite crystal is converted to amorphous SiO_2 and Al_2O_3 by heating at the temperature higher than 500°C. The electronmicrographs show that the external shape of the crystals is unchanged by this transition. No change in the shape is also observed on mixing into the rubber.

The reinforcing ability of a filler is related to the specific surface area of the particles. The larger the area, the higher the effect. It is quite natural that the reinforcement is caused by the mutual interaction between the rubber molecules and the filler. The fact that the heat-treatment at the temperature higher than 400°C decreased the reinforcing ability irrespective of the increase in the specific surface area suggests that the crystal structure of hard clay has more important bearings on the reinforcing effect than the specific surface area does.

As is shown in Fig. 10, kaolinite has a double-layer structure composed of tetrahedron of silica ($Si_4O_6(OH)_6$) and octahedron of $Al_2O(OH)_6$. The functional radical for the reinforcement of rubber is OH. According to Lyon and Tuddenham[6], the absorption peak of OH at 3700 cm^{-1} is due to 6(OH) at the bottom of $Al_2(OH)_6$ octahedron, and that at 3636 cm^{-1} to the OH of

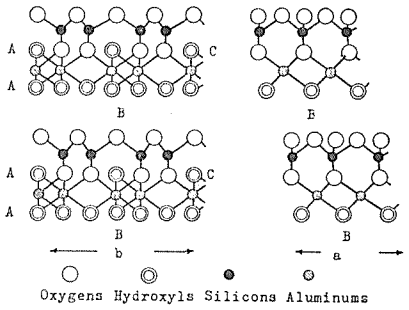


Fig. 10. Crystal structure of kaolinite (G. W. Brindley).

2(OH)+4O on the boundary layer of silica. The absorption at 3650 cm^{-1} was not observed by them. Marel and Zwiers[7] have studied the OH absorption band of various kaolinite minerals by using CaF_2 prism. They found cleary distinguishable for peaks of OH at 3698, 3660, 3630 and 3440 cm^{-1}. The assignments of these peaks made by then are : 3698 cm^{-1} OH on the lateral surface of crystal (A in Fig. 10) ; 3660 cm^{-1} OH on the bottom plane (B in Fig. 10) ; 3630 cm^{-1} OH on the octahedral layer (C in Fig. 10) ; 3440 cm^{-1} OH between the lattice planes. Taking account of these assingnments, it is concluded that the most intense absorption peak appearing at 3700 cm^{-1} among four bands found in the OH spectra of hard clay shown in Fig. 8 is of the OH on the lateral surface of crystal. This conclusion is confirmed by the fact halloystite or hydrated halloysite of similar crystal structure which is not in the shape of plane but of tube gives the absorption peak of lower intensity at 3700 cm^{-1}. The crystal structure of kaolinite shows that the OH on the lateral surface of the crystal is chemically most active.

The fact that the OH absorption band of kaolinite at 3700 cm^{-1} becomes weak on mixing in the rubber as is seen in Fig. 8 suggests the existence of some interaction between the OH radicals and the rubber molecules. It is concluded that the reinforcing effect of hard clay results from the strong chemical activity of OH on the lateral surface of the crystal of kaolinite. By the heat treatment of clay at the temperature higher than 400°C, the crystal structure of kaolinite is destroyed, and this active OH radicals are lost, resulting in the lowering of the reinforcing activity. Lower activity of clay minerals of similar crystal and chemical structure such as halloysite and hydrated halloysite is probably due to the fact that they possess smaller number of OH radicals on the lateral surface than the kaolinite does. The nature of interaction between the OH and the rubber molecules will be studied in future.

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